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## Phase identification of $\text{Al}_2\text{O}_3/\text{RE}_3\text{Al}_5\text{O}_{12}$ and $\text{Al}_2\text{O}_3/\text{REAlO}_3$ (RE = Sm–Lu, Y) eutectics

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### Abstract

Growth of various kinds of eutectic fibers based on  $\text{Al}_2\text{O}_3$  and oxides of Y and rare earths from Sm to Lu using micro-pulling-down ( $\mu$ -PD) method was investigated. The effect of rare-earth element substitution on growth, microstructure and mechanical properties are discussed. Eutectic materials were classified into  $\text{Al}_2\text{O}_3$ /garnet system and  $\text{Al}_2\text{O}_3$ /perovskite system types at the boundary between Gd and Tb.  $\text{Al}_2\text{O}_3$ /garnet eutectic fibers showed superior high-temperature strength properties. This is the first systematic study of the characteristics of these eutectic materials. © 2000 Elsevier Science B.V. All rights reserved.

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Keywords: Oxide eutectic; Fiber; Micro-pulling-down method; Microstructure

### 1. Introduction

The past four decades have seen an explosive development of eutectic composite materials. Directionally solidified superalloy metals were extensively investigated for structural applications at high temperatures, as in turbine blades. Many studies of eutectic solidification provided a basic under-

standing of the characteristics of those materials and a classification of various shapes of microstructure [1–3]. Subsequently, because of their high melting points, high strength at high temperatures, and resistance to oxidation, attention turned towards various ceramic eutectics [4,5] though difficulty in controlling the microstructure still prevented the formation of regular structure. Recently, promising results were obtained for the  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$  and  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  systems [6,7]. However, experimental data for oxide eutectics are still very limited. To understand the structural and mechanical properties, systematic investigation of these and related eutectic materials is needed.

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Up to now, a number of studies of binary  $\text{Al}_2\text{O}_3$ – $\text{RE}_2\text{O}_3$  systems (RE = rare earth) has been carried out. However, reports on eutectic structure and characteristics are mostly uncertain. For example, in Tb and some other systems, it has not been previously reported whether the rare-earth materials form a garnet phase, a perovskite phase, or a mixture of the two in a eutectic combination with  $\text{Al}_2\text{O}_3$ .

To remedy this situation, the present paper describes the systematic investigation of all  $\text{Al}_2\text{O}_3$ /RE–Al–O (RE = Sm–Lu, Y) eutectics, including complete identification of their phases and comparison of microstructure and tensile strength properties.

## 2. Experimental procedure

### 2.1. Starting materials and compositions

The starting materials and the compositions used in this work are listed in Table 1. These powders were dried, measured in proper proportions and mixed directly in the crucible. The eutectic composition of  $\text{Al}_2\text{O}_3$ / $\text{Y}_3\text{Al}_5\text{O}_{12}$  was taken from Ref. [8], and those of the other materials from Ref. [9].

Table 1

Starting materials and eutectic compositions

Starting materials	Purity	Supplier <sup>a</sup>	Eutectic composition (mol%)	
			$\text{Al}_2\text{O}_3$	$\text{RE}_2\text{O}_3$
$\text{Al}_2\text{O}_3$	5N	A		
$\text{Sm}_2\text{O}_3$	4N	B	74.0	26.0
$\text{Eu}_2\text{O}_3$	4N	B	75.0	25.0
$\text{Gd}_2\text{O}_3$	4N	A	76.0	24.0
$\text{Tb}_2\text{O}_3$	4N	B	78.0	22.0
$\text{Dy}_2\text{O}_3$	4N	B	80.0	20.0
$\text{Ho}_2\text{O}_3$	4N	B	80.5	19.5
$\text{Er}_2\text{O}_3$	4N	B	80.5	19.5
$\text{Tm}_2\text{O}_3$	4N	B	81.0	19.0
$\text{Yb}_2\text{O}_3$	4N	C	81.5	18.5
$\text{Lu}_2\text{O}_3$	4N	B	82.0	18.0
$\text{Y}_2\text{O}_3$	4N	A	81.3	18.7

<sup>a</sup>(A) High-Purity Chemicals Co., (B) Nippon Yttrium Co., (C) Shin-Etsu Chemical Co.

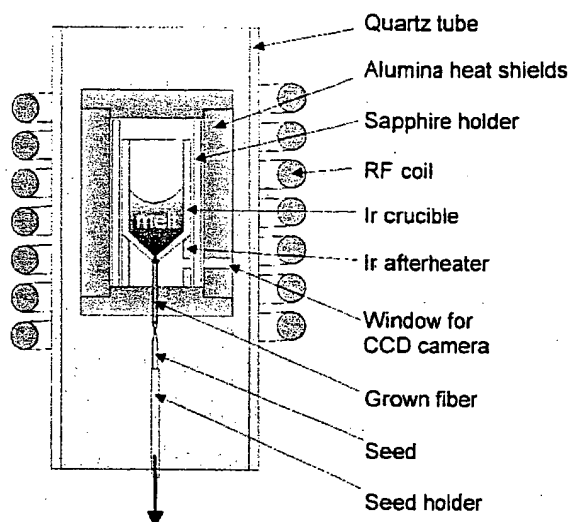


Fig. 1. Schematic diagram of the micro-pulling-down ( $\mu$ -PD) apparatus.

### 2.2. Fiber growth assembly and procedure

The eutectic fibers were grown by the micro-pulling-down ( $\mu$ -PD) method from an iridium crucible with a  $275\text{ }\mu\text{m}$   $\varnothing$  hole, as shown schematically in Fig. 1. Induction heating at a frequency of 5 kHz, specially designed for the fabrication of crystals and composites at high temperature (above  $1800^\circ\text{C}$ ), was employed. In order to observe the hanging meniscus and growing fiber during the experiments, small windows for a CCD camera are inserted in the afterheater and heat shield. The growth process was controlled manually by changing the pulling rate and heating power. The fibers were grown in Ar atmosphere (gas flow  $2\text{ l/min}$ ) to avoid oxidation of the crucible. This apparatus is described in greater detail in Refs. [10–12].

### 2.3. Evaluation techniques

To identify the phases present, powder X-ray diffraction analysis was carried out using a RAD-type X-ray diffractometer (XRD, Rigaku). A scanning electron microscope (SEM, Japan Electron) was used for the observation of microstructure of all samples. Back-scattered electron images (BEI) were used to distinguish the two phases. The tensile

strength tests were carried out using the high-temperature uniaxial tension-compression facility at Japan Ultra-high Temperature Materials Research Center (JUTEM). Tensile strength at 1500°C was measured using samples of 200 mm length; the applied tension was parallel to the fiber axis (pulling direction). The strain rate was  $10^{-4}$  N/s and tests were performed in vacuum to reduce the heat transfer to the Ti sample holder.

### 3. Results and discussion

#### 3.1. Phase identification

Oxides of rare earths from La to Pm have no eutectic point with  $\text{Al}_2\text{O}_3$ . For the eutectic forming materials, powder X-ray diffraction was measured to identify the phases. All peaks in each pattern were sharp and could be indexed. So it was found that these eutectic fibers were crystalline and contained no significant impurities. The nature of the rare-earth containing phase changed in going from Gd to Tb. Figs. 2(a) and (b) shows powder X-ray

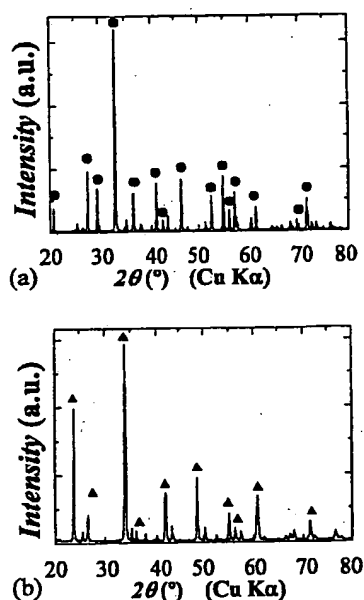


Fig. 2. Powder XRD pattern of pulverized (a)  $\text{Al}_2\text{O}_3/\text{Tb}_3\text{Al}_5\text{O}_{12}$  and (b)  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  eutectic fibers (●:  $\text{Tb}_3\text{Al}_5\text{O}_{12}$ , ▲:  $\text{GdAlO}_3$ , unmarked:  $\text{Al}_2\text{O}_3$ ).

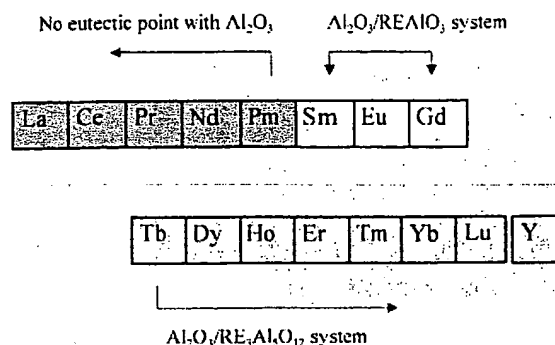


Fig. 3. Eutectic formation by rare-earth compounds and  $\text{Al}_2\text{O}_3$ .

diffraction patterns of  $\text{Al}_2\text{O}_3/\text{Tb}_3\text{Al}_5\text{O}_{12}$  and  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  pulverized fiber. Sm, Eu, and Gd showed  $\text{Al}_2\text{O}_3$  and a perovskite phase, while Tb–Lu showed  $\text{Al}_2\text{O}_3$  and garnet phase. No three-phase eutectic was observed. This agrees with and extends the previous research, which had not clarified completely whether garnet phase, perovskite phase, or a mixture of the two appeared in eutectics with  $\text{Al}_2\text{O}_3$ . According to the result of this work, the materials which form eutectics with  $\text{Al}_2\text{O}_3$  can be divided into the perovskite type and the garnet type at the boundary between Gd and Tb (see Fig. 3). No other type of eutectic with  $\text{Al}_2\text{O}_3$  was observed.

#### 3.2. Features of $\text{Al}_2\text{O}_3$ /garnet system

Fig. 4 shows the  $\text{Al}_2\text{O}_3$ /garnet system eutectic fibers obtained. In this system, reasonably stable growth was achieved over a wide range of pulling rates, 0.1–20 mm/min, with the highest achievable pulling rate being around 30 mm/min. The diameter of these fibers was well controlled in the range from 0.20 to 0.50 mm, and the length was 550 mm. The fibers were white or colored depending on the rare-earth ion. Fig. 5 shows a typical SEM image of the microstructure of  $\text{Al}_2\text{O}_3/\text{RE}_3\text{Al}_5\text{O}_{12}$  eutectic fiber. In all eutectic fibers in this system, the component phases formed a three-dimensional interpenetrating network known as Chinese script (CS) structure. It was completely homogeneous throughout the entire cross section of the grown fibers. The size of the domains was

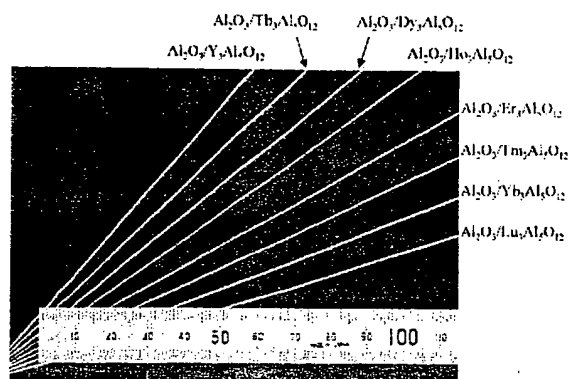


Fig. 4.  $\text{Al}_2\text{O}_3/\text{RE}_3\text{Al}_5\text{O}_{12}$  (RE = Tb–Lu, Y) eutectic fibers.

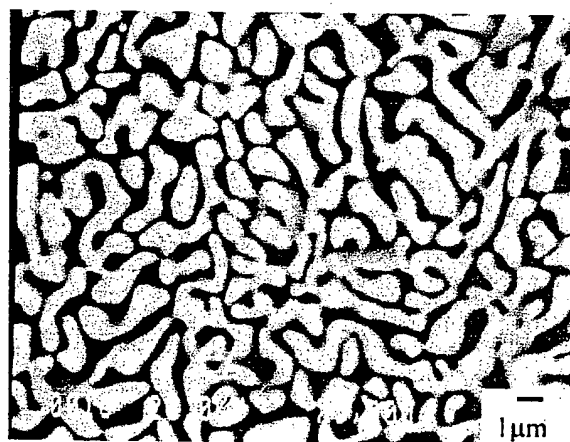


Fig. 5. SEM image of  $\text{Al}_2\text{O}_3/\text{Tb}_3\text{Al}_5\text{O}_{12}$  eutectic fiber cross section showing Chinese script microstructure. Other  $\text{Al}_2\text{O}_3/\text{garnet}$  materials had similar structure (dark region:  $\text{Al}_2\text{O}_3$  phase, bright region: garnet phase).

controlled by the growth speed, with high pulling rate producing smaller microstructure.

### 3.3. Features of $\text{Al}_2\text{O}_3/\text{perovskite}$ system

$\text{Al}_2\text{O}_3/\text{perovskite}$  system eutectic fibers were grown using Sm, Eu, and Gd (see Fig. 6). These materials behaved differently from the garnet system materials, and there were some problems during growth. For example,  $\text{Al}_2\text{O}_3/\text{SmAlO}_3$  easily disconnected from the melt during growth and this fiber could be grown only several centimeters in length. The maximum growth rate was 1.0 mm/min.

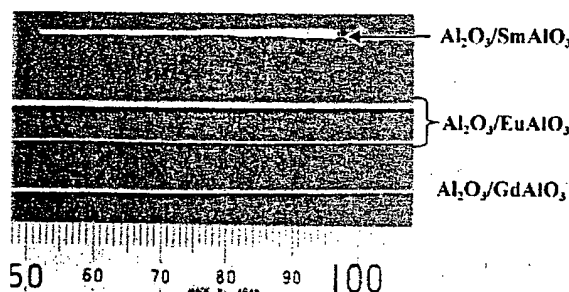


Fig. 6.  $\text{Al}_2\text{O}_3/\text{REAlO}_3$  (RE = Sm–Gd) eutectic fibers.

$\text{Al}_2\text{O}_3/\text{EuAlO}_3$  exhibited more stable growth, and fibers could be grown at a pulling rate up to 15 mm/min. Very thin fibers (around 100  $\mu\text{m}$ ) could be grown, but it was difficult to control the diameter, and the thin fibers easily got disconnected. In the case of  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$ , fibers could be grown at a pulling rate up to 15 mm/min, but this material very easily bent during growth. Fig. 7 shows typical SEM images of microstructure of  $\text{Al}_2\text{O}_3/\text{REAlO}_3$  eutectic fiber in cross section and longitudinal section. It was found that the microstructure in this system was not uniform, but rod-shaped colonies were mixed with regions of Chinese script (CS). The ratio of the volumes of the rod-shape and CS structure varied and only a small number of samples from fibers grown at low growth rate exhibited uniform CS structure.

### 3.4. Off-eutectic composition

To examine how the stability and homogeneity of the microstructure in  $\text{Al}_2\text{O}_3/\text{garnet}$  and  $\text{Al}_2\text{O}_3/\text{perovskite}$  systems are influenced by chemical composition, off-eutectic growth was attempted. Fibers were grown with chemical composition shifted from the eutectic point by several mole percent. Figs. 8 and 9 show the resulting microstructure of  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$  and  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  eutectic fibers. The homogeneity of the CS texture in  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$  was unchanged. In the case of  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$ , the change in composition strongly affected the structure: a decreased fraction of  $\text{Gd}_2\text{O}_3$  increased the amount of rod-like microstructure relative to the amount of CS microstructure. A detailed understanding of the

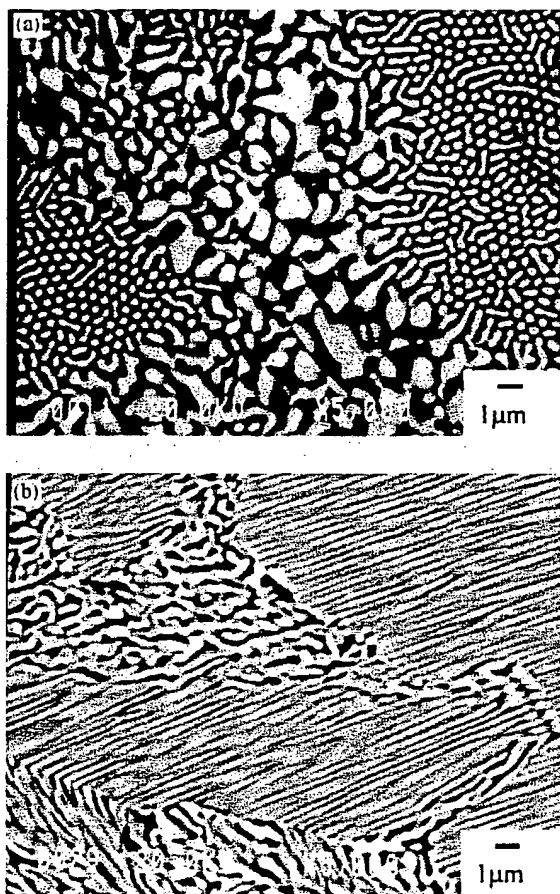


Fig. 7. SEM image of  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  eutectic fiber perpendicular and parallel to the growth direction showing regions of rod-like and Chinese script type microstructures. Other  $\text{Al}_2\text{O}_3$ /perovskite fibers had similar microstructure (dark region:  $\text{Al}_2\text{O}_3$  phase, bright region: perovskite phase).

microstructure formation is still lacking, but we can rationalize some aspects of the difference between CS and rod-shaped microstructure in the following way. As reviewed by Minford et al. [13], the basic microstructures of eutectics are correlated with the relative interfacial surface area per unit volume for the fibrous or rod-like and lamellar forms. A fibrous structure has lowest surface energy when the volume fraction of the minor phase is  $< 0.28$ . Otherwise, the microstructure tends to be lamellar. The  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  eutectic, for example, which falls near the division point, has been observed to form both rod-shape and lamellar microstructure. The

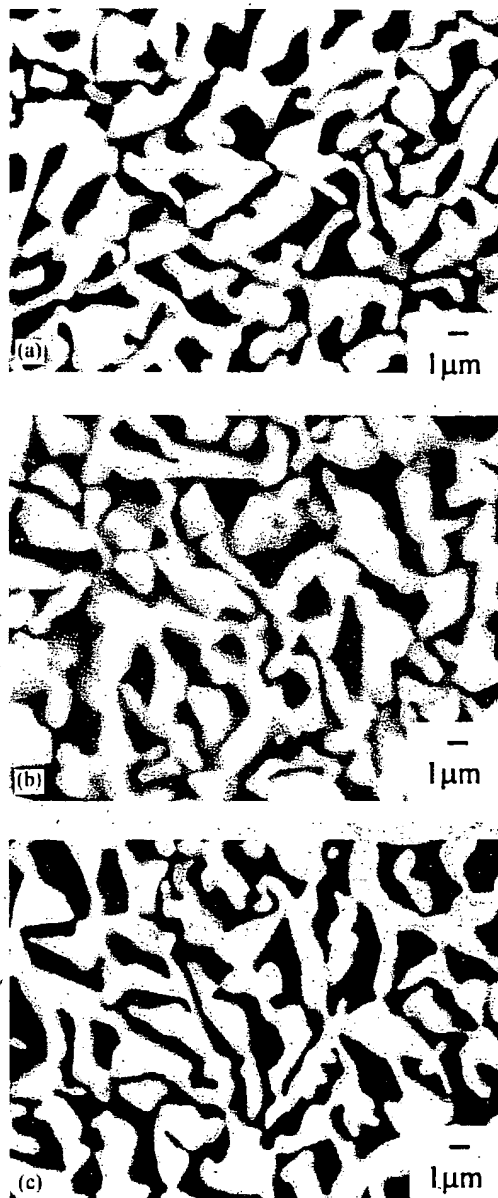


Fig. 8. SEM images of cross section of  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$  eutectic fibers grown from different starting compositions.  $\text{Al}_2\text{O}_3:\text{Y}_2\text{O}_3 =$  (a) 76.3:23.7, (b) 81.3:18.7, and (c) 86.3:13.7 (dark region:  $\text{Al}_2\text{O}_3$ , bright region:  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ).

change of microstructure in  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  qualitatively follows this tendency. The volume fraction of  $\text{GdAlO}_3$  in the  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  eutectic as measured on digitalized images, was 0.38 in rod-shaped

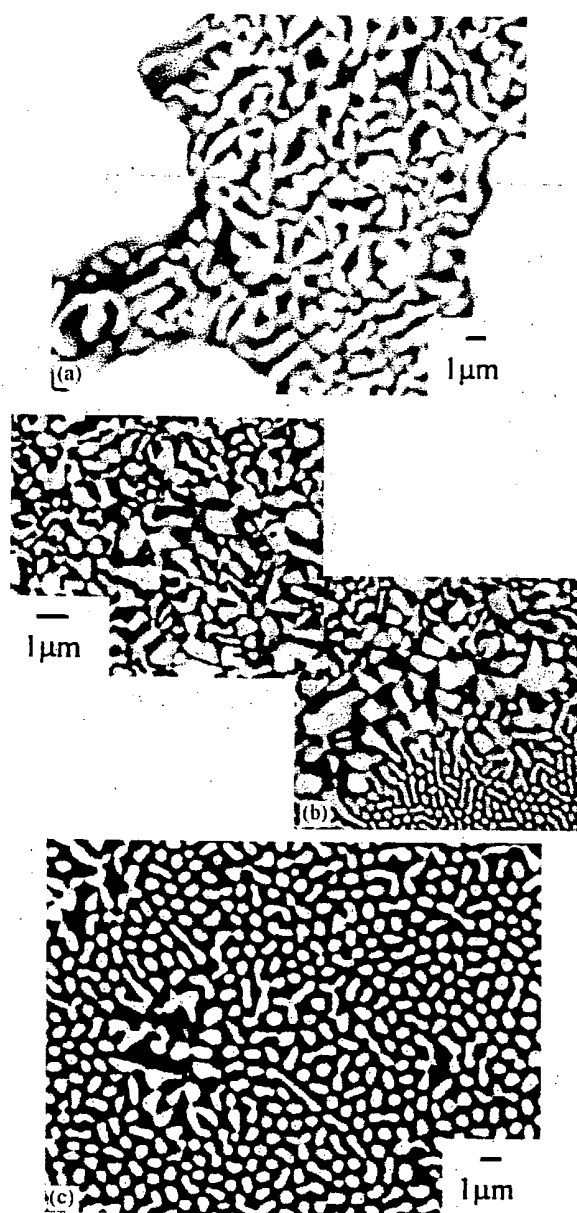


Fig. 9. SEM images of cross section of  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  eutectic fibers grown from different starting compositions.  $\text{Al}_2\text{O}_3:\text{Gd}_2\text{O}_3 =$  (a) 72:28, (b) 73:27–76:24, and (c) 77:23 (dark region:  $\text{Al}_2\text{O}_3$ , bright region:  $\text{GdAlO}_3$ ).

regions, but approached 0.50 in CS regions of fibers grown from  $\text{Gd}_2\text{O}_3$ -rich composition. The cross-over volume fraction is very different from that for

the rod-lamellar transition, presumably for the same reason that these materials form Chinese script rather than simple lamellar microstructures. We note that  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$  formed CS structure even when the volume fraction of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  to  $\text{Al}_2\text{O}_3$  was over 0.62. It seems that other factors, for example facet or non-facet behavior of the material can also affect the type of microstructure.

### 3.5. Tensile strength

To investigate the mechanical characteristics of grown eutectic fibers, tensile stress-displacement tests were carried out. Tensile strength data for eutectic fibers grown at 15 mm/min are listed in Table 2.  $\text{Al}_2\text{O}_3/\text{garnet}$  system eutectic fibers remained strong at 1500°C.  $\text{Al}_2\text{O}_3/\text{Tm}_3\text{Al}_5\text{O}_{12}$  (624 MPa) was the strongest among these, and was more than three times stronger than bulk  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$  material. The  $\text{Al}_2\text{O}_3/\text{perovskite}$  system eutectic fibers, which had colony type microstructure, had about half the strength of  $\text{Al}_2\text{O}_3/\text{garnet}$  eutectic fibers. Uniform microstructure has been shown to be necessary for best mechanical properties; it is possible that  $\text{Al}_2\text{O}_3/\text{perovskite}$  system eutectics would be stronger if the microstructure could be made uniform.

## 4. Conclusions

We have successfully grown many possible  $\text{Al}_2\text{O}_3/\text{RE-Al-O}$  (RE = rare earth) eutectic fibers using the  $\mu$ -PD method, many for the first time. It was found that the materials which form eutectics with  $\text{Al}_2\text{O}_3$  can be divided into the perovskite type and the garnet type at the boundary between Gd and Tb.  $\text{Al}_2\text{O}_3/\text{garnet}$  system eutectics showed uniform Chinese script microstructure, while rod-shaped colonies mixed with the CS structure were observed in  $\text{Al}_2\text{O}_3/\text{perovskite}$  systems. The latter type of microstructure was strongly influenced by the chemical composition.  $\text{Al}_2\text{O}_3/\text{garnet}$  system eutectic fibers showed high tensile strength: 624 MPa at 1500°C, for the case of  $\text{Al}_2\text{O}_3/\text{Tm}_3\text{Al}_5\text{O}_{12}$ . This is the highest value reported at this temperature for any material.



Table 2

Tensile strength of various eutectic fibers grown at 15 mm/min

Eutectic fibers	Strength at 1500°C (MPa)	Eutectic fibers	Strength at 1500°C (MPa)
$\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$	552	$\text{Al}_2\text{O}_3/\text{EuAlO}_3$	315
$\text{Al}_2\text{O}_3/\text{Dy}_3\text{Al}_5\text{O}_{12}$	564	$\text{Al}_2\text{O}_3/\text{GdAlO}_3$	277
$\text{Al}_2\text{O}_3/\text{Ho}_3\text{Al}_5\text{O}_{12}$	551		
$\text{Al}_2\text{O}_3/\text{Er}_3\text{Al}_5\text{O}_{12}$	559	$\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$ bulk (Bridgman)	200
$\text{Al}_2\text{O}_3/\text{Tm}_3\text{Al}_5\text{O}_{12}$	624		
$\text{Al}_2\text{O}_3/\text{Yb}_3\text{Al}_5\text{O}_{12}$	572		
$\text{Al}_2\text{O}_3/\text{Lu}_3\text{Al}_5\text{O}_{12}$	447		

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# prices

The prices obtained vary widely according to type, source, quality, quantity purchased and the application. Hence the following quotations can only serve as a guide to the prices obtained by producers and dealers. All units are metric tonnes, unless otherwise stated. To accord with trade practices, most prices are quoted in US\$. All quotations are ©Metal Bulletin plc 2001.

## bauxite

Chinese refractory bauxite, min.87%  $Al_2O_3$ , typical BD 3.15, FOBT

Shanxi, shaft,lump.....	\$71-78
rotary, lump.....	\$85-90
Guizhou, round, lump.....	\$70-75
Guizhou, rotary, lump.....	\$85-90

## boron minerals

Turkish lump colemanite, FOB, 40-42%  $B_2O_3$ ,

USA/Japan.....	\$270-290
Europe.....	DM490-505
Argentinian colemanite, 40-42% $B_2O_3$ , ground, bagged, FOB Argentina.....	\$400-450
Latin American ulexite 40% $B_2O_3$ , FOB Lima.....	\$220-250

## chromite

South African friable lumpy, basis 40% $Cr_2O_3$ , FOB.....	\$40-55
Albanian, lumpy, 42-47% min., FOB.....	\$65-70
Turkish concentrate, 48% min., FOB.....	\$75-85
Kazakhstan, 40-41% min.,	\$105-235
Kazakhstan, 48% .....	£135-155

## feldspar

Ex-works USA, s.ton, bulk	
- ceramic grade, 170-200 mesh (Na).....	\$61-73
200 mesh (K).....	\$126
glass grade 30 mesh (Na).....	\$40-50
40 mesh (K).....	\$85-90

## iron oxide pigments

Ochre, FOB USA, CL/TL s.ton, cents per lb	
light.....	\$0.21
medium.....	\$0.17
dark.....	\$0.15

## kaolin

ex-Georgia plant, short ton	
sanitaryware grade, bagged.....	\$62-72
tableware grade, bagged.....	\$134
calcined, bulk.....	\$356-418
refined, FOT, ex-Cornwall, UK	
ceramic grade.....	\$39-101
porcelain grade.....	\$89-144

## lithium minerals

petalite, 4.2% $Li_2O$ , big bags, FOB Durban.....	\$180-270
spodumene concentrate >7.25% $Li_2O$	
FOT Amsterdam.....	\$385-395
FOB West Virginia., short ton, bulk.....	\$330-350
glass grade spodumene, 5% $Li_2O$	
FOT Amsterdam.....	\$200-210
FOB West Virginia, short ton, bulk.....	\$195-200
lithium carbonate, delivered continental USA	
bags or drums, per lb (list).....	\$1.97-2.03
large contracts, per lb.....	\$0.94-1.20

## manganese

chemical grade 74-84% $MnO_2$ , unground, bulk CIF Europe.....	\$140-250
chemical grade, 74% $MnO_2$ , 200 mesh bulk ex-works .....	\$275-340

## nepheline syenite

Canadian, short ton:	
glass, 30 mesh, bulk, low iron.....	\$32
glass, 30 mesh, bulk, high iron.....	C\$29-30
ceramic, 200 mesh, bagged 1 ton lots.....	C\$85-90
Norwegian, FOL UK port	
glass grade, 0.5mm bulk.....	£97
ceramic grade 45µ, bulk.....	£114
ceramic grade 45µ, bulk.....	£145

**pyrophyllite**

Milled, filler grade, FOB Australia .....	\$342
Filler grade (21-27% $Al_2O_3$ ), FOB South Korea.....	\$110-150
Ceramic grade, (15-19% $Al_2O_3$ ), FOB South Korea.....	\$27-44

**rare earth minerals**

bastnaesite concentrates, 70% leached, per lb.....	\$2.25
yttria (99.99% $Y_2O_3$ ), kg.....	\$13-16

**refractory clays**

Chinese flint clay, 45% $Al_2O_3$ , FOB China.....	\$77
European calcined kaolinitic, 47% $Al_2O_3$ , clay, FOB.....	\$115-125
Mulcoa products, 47% $Al_2O_3$ , FOB USA, kiln run, per s.ton.....	\$84

**soda ash**

US natural, FOB Wyoming, dense, short ton.....	\$105-115
large contract.....	\$74-84
European synthetic, ex-works, dense & light, contract.....	€140-150

**talc**

Norwegian, ground (ex-store) UK.....	£142-90
Norwegian, micronised (ex-store) UK.....	£220-294
Chinese normal, ex-store UK, 200 mesh.....	£200-225
Chinese normal, ex-store UK, 350 mesh.....	£210-230

**wollastonite**

US ex-works, short tons:	
acicular -200 mesh.....	\$190
325 mesh.....	\$234
400 mesh.....	\$258
acicular (15:1-20:1 aspect ratio).....	\$318

**zircon flour**

CFR Asia.....	\$420-480
FOB Malaysia.....	\$510-540

**zircon opacifier**

C&F Asia.....	\$580-640
CIF China.....	\$760-825

**zircon sand**

FOB bulk, Australia.....	\$315-345
FOB bulk, USA.....	\$345-375
FOB India.....	\$330-420

The cost of some US produced ceramic grade feldspar products increased at year end 2000. Sodium ceramic feldspar is currently \$61-73/s.ton, ex-works eastern USA (170-200 mesh, bulk), having undergone a rise of about \$3/s.ton during December 2000. Lower range prices for bagged material have risen by \$9/s.ton, while upper range values have reportedly edged upwards by about \$1/s.ton, from \$75-95/s.ton, ex-works eastern USA, to \$84-96/s.ton. Potash ceramic grade feldspar (200 mesh, bagged) has increased in price by \$6/s.ton, standing at \$126/s.ton, ex-works eastern USA, for December. Meanwhile, glass grade product has also been effected by price rises for 2001. Sodium feldspar (bulk, 30 mesh) for the glass industry has seen a \$2/s.ton increase in the upper pricing range and is currently selling at \$40-52/s.ton, ex-works eastern USA.

Following a \$5/s.ton price rise late in the third quarter of last year, the major US soda ash producers implemented a further increase in December 2000. Energy costs have remained high and this has been the primary factor behind the latest \$5/s.ton hike of off-list prices. For January 2001, the cost of US soda ash is \$74-84/s.ton, bulk, FOB Wyoming (dense, contract price). List price values for North American material are stable at \$105-115/s.ton, bulk, FOB Wyoming, as is the cost of Chinese synthetic soda ash, which is presently \$85-95/tonne, FOB China (light and dense). Prices for Chinese product on a CIF Far East basis were \$115-125/tonne during December 2000.

After a lengthy dispute between ANSAC and the Indian authorities, India's Ministry of Commerce has recommended anti-dumping duties on soda ash imports from Japan, France, Iran, Saudi Arabia and the USA. Reports have indicated that US soda ash exporters can expect to pay a duty equalling the difference between \$345.44/tonne and the landed values of the imported product.

Zircon sand prices have crept upwards by about \$5/tonne for 2001. Ceramic grade material values are now in the range of \$315-345/tonne, bulk, FOB Australia. Meanwhile, the cost of zircon opacifier and flour in the Asian market has been firming up. Micronised zircon is currently about \$580-640/tonne, CFR Asia, compared with \$560-630/tonne for Q4 2000. While some sources have reported that lower values for these products are available, they point out that the present market trend is towards firmer pricing.

*Lindsey Taylor*

Lindsey Taylor is Deputy Editor, Mineral PriceWatch. For a free sample copy contact the Asian Ceramics and Glass marketing department



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Article 58

### Rare earths: an industry review and market outlook - part I [2 tables]

12/08/2000

Chemical Business NewsBase: Elements

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The global rare earths industry places emphasis on the exploitation of bastnasite, monazite and xenotime, currently the only three minerals that contain commercially significant amounts of rare earths.

Bastnasite has roughly 7-10% **rare earth** oxides and minor amounts of yttrium.

Among the major bastnasite deposits being mined are in Wigu Hill, Tanzania; Bayan Obo, China; Mountain Pass, CA; and Karonge, Burundi.

Monazite has roughly 70% **rare earth** content.

Major monazite deposits can be found in Bahia and Espirito Santo in Brazil, Tamil Nadu and Kerata in India, and along the coasts of Western Australia.

Xenotime, which contains significant levels of yttrium, is mined in Indonesia, Australia, Thailand and Malaysia.

Global reserves of rare earths reach an estimated 100 M tonnes.

China leads in **rare earth** reserves with an estimated 43 M tonnes or roughly 80% of the world's recoverable rare earths.

Molycorp's Mountain Pass resource has the highest-grade commercial bastnasite deposit, containing reserves of 4.3 M **rare earth** oxides.

Global rare earths production reached an estimated 76,500 tonnes in 1999, down 100 tonnes compared in 1998.

China is the leading rare earths producer, accounting for almost 90% of 79,000 tonnes of contained rare earths currently produced globally.

However, Chinese rare earths production has dropped in 2000, with observers saying that local governments China have reduced production to boost rare earths **prices**.

The declining trend in production is also observed in other global regions.

Brazilian and Norwegian rare earths production has stopped.

The Molycorp Mountain Pass mine in California has also been temporarily shuttered.

Among the major companies involved in rare earths production are Rhodia Ltd, Ashton Rare Earths Pty Ltd and Baxton Steel & Rare Earth Co.

Ashton Rare Earths Pty Ltd and Baotou Steel & Rare Earth Co.

Rhodia, the leading producer of separated rare earths, is set to gain access to a 9000 ton/y of **rare earth** production capacity via a JV with Chinese companies Liyang Licheng Economic General Industrial Co Ltd and Beijing BeiDa Group.

Ashton Rare Earths is set to finish a feasibility study of the Mt Weld/Meenaar **rare earth** project in Australia in Nov 2000.

The project is expected to have a 30-year life span and produce up to 20,000 tonnes/y of concentrates with 40-50% **rare earth** oxides.

China's Baotou Steel & **Rare Earth** holds 77% of the world's **rare earth** reserves.

Website: <http://www.rareearthsmarketplace.com>

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## Rare Earth

## Market Confusion Inevitable Due to China's Unstable Supply

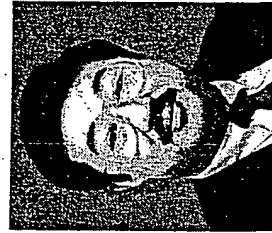
Domestic production volume of rare earth in 1999 increased by 8% year-on-year to 5,092 tons. Imports of rare earth products, including both raw material and intermediates, increased by 12% over the previous year to 23,000 tons in volume but decreased by 22% in value to ¥17.8 bn (\$170 mn).

This is because the increase in volume was brought about by cheap rare earth products imported from China, while they lowered the unit price of imports, causing a larger drop in value that offset the volume increase.

Exports of rare earth products, led by cerium compounds, amounted to ¥5.5 bn, up 83% over the previous year. Making a good contrast with imports from China, which show an inclination toward low prices, exports from Japan are growing in terms of both volume and value, while increasing in added value.

### Phosphor, Abrasives and Catalysts-Ce, La, Y, Eu

Cerium oxide imports increased in volume by 17% year-on-year to 3,606 tons, but they registered a 19% decrease in value. Imports of cerium concentrate as an intermediate product ended at 5,152 tons, a 1% increase in volume, but a 25% decline in value from the previous year.



S. Nakamura  
Chori Co.

The market for rare earth for abrasive and catalyst applications continued to be active throughout 1999. Lanthanum oxide imports were 988 tons, registering an increase of 30% in volume, but a decrease of 33% in value.

Yttrium oxide and europium oxide for phosphor applications also showed similar tendencies, recording a hefty 45% increase in import volume at 756 tons, but a 14% decline in value. This means that product imports are increasing at an accelerated pace in the phosphor application area, indicating Japan's increasingly hollowed-out rare earth industry.

From the above data, it can be said the rare earth market has bottomed out and that demand has begun to pick up in the respective areas.

### Magnetic Material and Capacitors-Nd, Pr, Dy, Sm

Magnetic materials, led by NdFeB, maintained steady growth continuing from the previous year. Their prices are showing a tendency to rise in 2000 due to raw material short supply. Rare earth imports in 1999 ended at 4,659 tons, registering a 25% increase in volume (including misch metal) year-on-year, but a 19% decline in value.

China's production volume of NdFeB (including both sintered and

bonded products) and Sm-Co magnet in 1999 surpassed that of Japan, recording 5,180 tons for NdFeB. China is expected to increase its production by 20% or more every year in the future. Accordingly, the market trend of Nd metal and Dy metal, major raw materials, needs to be watched carefully in 2000.

### Rechargeable Batteries-Misch Metal

Demand for hydrogen occlusive alloys for Ni-MH batteries expanded to 5,500 tons, recording growth of more than 20% over 1998. Though mobile phones and PCs primarily use lithium ion batteries, electric vehicles are expected to use Ni-MH batteries, suggesting the possibility of continuing 10% growth in the future.

Japan's rare earth market has changed its structure from time to time during its history, starting from raw material imports focusing on monazite and rare earth chlorides in the 1970s. Then the market shifted its weight to extraction and separation, primarily from concentrates as rare earth intermediates in the 1980s.

In the 1990s, however, due to the hollowing-out starting in the rare earth separation industry, the market began to increase imports in the forms of separated rare earth products and rare metals from China at an astonishing pace.

Following such market trends, Japanese rare earth producers have transformed themselves into refiners capable of catering for diversified applications, specializing themselves in highly value added rare earth products for advanced application areas.

In 2000, demand growth is expected from new application areas including condensers, semiconductors

and memory materials, to say nothing of batteries, magnetic materials and phosphors.

### China's Market

One must refer to an analysis of the relation between the Japanese and Chinese markets in discussing rare earth supply and demand. China's rare earth ore production in 1999 increased to 106,600 tons (about 70,000 tons as RED), up about 8% over the previous year.

Production volume of separated rare earth products was about 60,000 tons, up 11%, and export volume, about 50,000 tons, were up 10%. In spite of the increase in export volume, export value (\$460 mn) declined.

More than 90% of over 5,000 rare earth plants scattered in China fell into the red, and small and medium-scale rare earth plants were either closed or liquidated. Due to this distressed state of the industry, the Chinese government has made its decision to further enhance control of the rare earth export and to streamline rare earth mines and plants in a bid to reform the domestic market into a more orderly one.

More specifically, the government implemented production curtailment by 20% starting in January 2000 at a rare earth ore dressing plant in Baotou and a 10% price hike. It also put similar production curtailment into execution for ion-absorptive ores in the Jiangxi Province in its effort to tighten the market.

As a result of these moves, the export of rare earth in the form of raw material or the like was suppressed, while the export of more value-added products was promoted. Even in the first half of 2000 alone, the neodymium oxide price rose from \$7/kg to \$11/kg and metal neodymium, from

\$10/kg to \$16/kg. In addition, an unusually keen appreciation in price from \$60/kg to near \$100/kg has been observed with Dy metal.

If the present market trend continues, prices are bound to rise in the second half of 2000 again. As China's participation in WTO is drawing near, the rare earth-related industries are beginning to feel a sense of crisis. China's adjustment of its stance and measures to stabilize the market are desirable.

Based on the prospects of Chinese supply mentioned above and demand from the Japanese market, it looks as

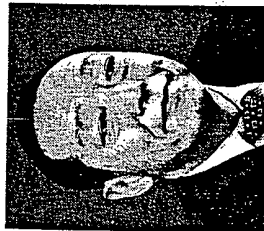
### Life Science

## Bio-Tech Revolution Involves Pharmaceutical Industry

The rapid growth of the life science industry is one of the remarkable moves observed in 1999 through 2000. Life science has begun to demand a new framework for business promotion as a separate segment to trading houses, which regarded it as a part of the fine chemicals segment until recently.

This is solely because a new horizon is beginning to be opened for the bio-industry by the completion of the decipher of the human genome and resultant elucidation of a tremendous volume of information.

In the first biotechnology boom in the 1980s, the establishment of genetic engineering as a new technique opened the way primarily for industrial and commercial production of



R. Ogawa  
Mitsui & Co.

functions of each gene.

Looking to pharmaceutical companies in Japan in this context, it cannot be denied that they are rather behind multinational pharmaceutical giants in terms of their attitudes in absorbing achievements made by American or innovative venture businesses, as has been pointed out by many industry observers.

if year 2000 will stage the revision of price levels, a rare occasion that happens, say, once in ten years. In other words, unstable Chinese rare earth supply and increasing demand from the Japanese market will throw the market off balance, and market confusion attracting speculations looks unavoidable.

China's resources and the Japanese market deserve a closer link, but how long will it take to establish a firm relationship between the two?

*Shigeo Nakamura, General Manager, Materials Dept., Chori Co., Ltd.*

Under these circumstances, the Japanese government now wants to expand the bioindustry's market to ¥25 trn (\$238 bn) in size by 2010 by enhancing industry, academic and government cooperation as well as providing ample funds (¥230 bn secured as the life science related budget).

Accordingly, we should wait and see whether bio ventures will also grow in Japan based on industry, academic and government cooperation in the next ten years. Hopefully, venture businesses will emerge out of spin-offs supported by large enterprises.

The gap, however, that exists between the Japanese and American environments for venture businesses today is significant, and hence the government is striving to improve environmental conditions including the capital market, investment funds and consulting services.

All living species on this earth have the same language genetically; fungi, plants, animals and the human race have it as DNA sequences. Like the IT (information technology) industry, which flourishes on the basis of digital signals, i.e., "0" and "1," the BT (bio-technology) revolution is expected to start soon, based on DNA sequences as its key words and involving the fermentation, agricultural, food (feed stock and meat), agrochemical, pharmaceutical and other industries.

*Ryu Ogawa, General Manager, Life Science Division, Specialty Chemicals & Plastics Group, Mitsui & Co.*

### Competition in Asian —

(Continued from Page 4)

the domestic market, but with the

coming of global competition, thorough reinforcement of cost competitiveness is now required.

### Further Restructuring Needed

As a measure to enhance cost competitiveness, business integration moves have surfaced. As a result of integrations, the companies have succeeded in improving their competitiveness and their business structures through payroll reduction, concentration of production, reduction of distribution costs, and improvement in business practices.

The major Western chemical manufacturers, however, are pushing forward with business integrations, M&A (merger and acquisition), and expansion of overseas production, mainly in Asia, at an even faster pace than the Japanese chemical companies are. Furthermore, they are realizing drastic changes in their operational strategies, including a shift of emphasis to the life science businesses, such as pharmaceuticals and agricultural chemicals based on gene recombination and other leading-edge technologies.

The Japanese companies, in comparison, have suffered from the slump in the Southeast Asian economy since the latter half of 1997, as well as the recession in the Japanese economy following the domestic financial system crisis, problems that have almost completely offset the effects of their past restructuring efforts.

It is not too much to say that they are still facing an urgent need for thorough restructuring, including further reduction in labor costs, concentration of production, and revision of their business structures.



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# Japan Chemical Week

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## Bayer to Invest \$4 Bn in PU Material in Asia over Ten Years

Seizing the opportunity afforded by its acquisition of Lyondell's polyols business, Bayer will go on the offensive in its Asian polyurethane (PU) feedstocks business.

This was revealed in a press conference given by the company's Polyurethanes Business Group in Singapore, when Hans J. Kaiser, general manager of the business group, outlined an aggressive target: "We will invest \$4 bn by 2010, and will increase our present approximately 10% share of the Asian market to 25% by 2005 at the latest."

In isocyanates, construction of plants for TDI and MDI with capacities from 160,000 to 230,000 t/y is under study, and plans are already



Bayer Polyurethanes in Asia - Activities in a Fascinating Market" Singapore, June 22.

Thrust deep into the polyurethane material business: Executives of Bayer Polyurethanes Business Group at a Singapore press conference.

being refined around five candidate sites. Kaiser said the intention is "to reach a provisional go/no go decision on one of the two plans before the end of the year."

Meanwhile, the acquisition from

Lyondell has greatly reinforced the company's polyols position in Asia. Besides securing production locations in Kaohsiung, Taiwan and Anyar, Indonesia, a technical center in Singapore has also been acquired.

Production capacity in Taiwan is approximately 45,000 t/y, while in Indonesia it is about 32,000 t/y. However, "We will undertake 50% capacity increases at both sites, introducing new technology acquired from Lyondell, etc."

The raw material position will also be boosted. Negotiations are already in progress with Lyondell with a view to constructing a 285,000-t/y propylene oxide (PO) plant at Rotterdam. A further objective is to secure a PO supply base in Asia.

Bayer has taken the decision to set up in Japan and Singapore a regional headquarters in the polyurethanes business. Reinhard Clausius, Head of Marketing, Polyurethanes Business Group said "The Japan regional head-

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### Nippon Steel Chem to Build 100,000-t/y BPA Unit in Korea

Nippon Steel Chemical will form a joint venture in South Korea with Korea Kumho Petrochemical and three affiliates of Kumho, after receiving the transfer of properties, including phenol and bisphenol A (BPA) plants, and related businesses from Kumho Development, a Kumho Group company.

In addition to the BPA plant to be transferred, the joint venture will build a new BPA plant, with an expected capacity of 100,000 t/y. Production start-up is targeted for two years' time, when a severe shortage of BPA supply is expected. The new firm will aim at sales of ¥18 bn (\$171 mn) in 2000 by expanding sales in Asia.

The joint venture, named Kumho P&B Chemical, will commence busi-

### E-Commerce Gears Up for Growth

## 4 Major Traders Set Up Two New EC Companies with ChemConnect

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